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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention is a rubber constituent which contains a silica system bulking agent in detail about a rubber constituent, and after hardening is related with the rubber constituent which may become the rubber Plastic solid excellent in rubber elasticity and the mechanical strength.

[0002]

[Description of the Prior Art] Conventionally, the organic system rubber which carbon black was blended [ rubber ] with organic system rubber, such as styrene / butadiene copolymer rubber, a polybutadiene rubber, and natural rubber, and reinforced intensity as rubber currently used for pneumatic tires, such as an automobile and a bicycle, is used. However, a part or all of carbon black is transposed to a silica system bulking agent, and the attempt which obtains vulcanized rubber excellent in mechanical strengths, such as rubber elasticity \*\*\*\*, a tear strength, elongation at the time of fracture, and abrasion resistance, is performed in recent years. However, generally, when it did not have compatibility to organic system rubber but this was blended with organic system rubber, it was difficult for the silica system bulking agent for silica system bulking agents to condense and to obtain the organic system rubber constituent which the silica system bulking agent distributed uniformly. Therefore, the method of using an organosilane together at the time of combination of a silica system bulking agent is proposed. For example, the method of blending a silica impalpable powder and a chlorine atom content organosilane with styrene / butadiene copolymer rubber, and obtaining a rubber constituent is proposed by JP, 58-36009, B. Moreover, the method of blending a silica impalpable powder and a sulfur atom content organosilane with styrene / butadiene copolymer rubber, and obtaining a rubber constituent is proposed by JP, 59-15940, B, and it is in it. however, the thing acquired for the constituent which the silica system bulking agent distributed uniformly even if it follows these methods -- hard -- the rubber Plastic solid which has a physical property good as a result -- it can obtain -- \*\*\*\*\*

[0003]

[Problem(s) to be Solved by the Invention] In order to cancel the above-mentioned trouble, as a result of inquiring wholeheartedly, the silica system bulking agent found out distributing uniformly in organic system rubber, and this invention persons resulted in this invention, when using together a silica system bulking agent and specific organopolysiloxane resin. That is, the purpose of this invention has the good dispersibility to the inside of the organic system rubber of a silica system bulking agent, and after hardening is to offer the organic system rubber constituent which may serve as a rubber Plastic solid excellent in rubber elasticity and the mechanical strength.

[0004]

[Means for Solving the Problem] this invention (A) organic system rubber The 100 weight sections, (B) silica system bulking agent The 5 - 180 weight section, (C) carbon black bulking agent The 0 - 200 weight section, the (D) silane coupling agent 0.1 -- -- ten -- a weight -- the section -- (-- E --) -- an average -- an empirical formula -- :  $(R_1SiO_{3/2})_m - [(R_2Si(OR_6)O_{2/2})_n] - R$  -- three -- Si

(OR7) -- two -- O -- one -- /-- two --] -- p (R4R5SiO 2/2) -- q (R9R10SiO1 / R1, R2, R3, R4, R5, R9, and R10 The monatomic organic group chosen from the amino alkyl group of a 12 or less-carbon number monovalent hydrocarbon radical, the 1st class, the 2nd class, or the 3rd class, an epoxy alkyl group, a meta-chestnut ROKISHI alkyl group, a mercapto alkyl group, and an alkyl-halide machine is shown. R6, R7, and R8 show a 12 or less-carbon number monovalent hydrocarbon radical or a hydrogen atom. m is the integer of 5-1,000, and n and p are the number of 1-1,000, and the sum of n, m, and p is 180 or more.

q is the integer of 20-1,000 and r is the number of 0-1,000. Organopolysiloxane expressed 0.1 - 10 weight section and (F) vulcanizing agent It is related with the rubber constituent characterized by the bird clapper from sufficient amount to stiffen the (A) component.

[0005] Generally the organic system rubber of the (A) component used in this invention is the organic high molecular compound which may become the bridge formation object which is called organic system rubber, constructs a bridge and has rubber elasticity, and especially the kind etc. is not limited. As this organic system rubber, styrene / butadiene copolymer rubber, a polybutadiene rubber, SHISU-polybutadiene copolymer rubber, styrene / isoprene copolymer rubber, styrene / isoprene / butadiene copolymer rubber, acrylonitrile / butadiene copolymer rubber, polyisoprene rubber, and natural rubber are mentioned.

[0006] The silica system bulking agent of the (B) component used for this invention is a reinforcement nature bulking agent. As for this silica system bulking agent, what is generally used as reinforcement nature bulking agents, such as organic system rubber, is usable, and especially the kind etc. is not limited. As this silica system bulking agent, the loadings of this component to which wet method silicas, such as dry-process silicas, such as a fumed silica, and a sedimentation silica, are mentioned are the 5 - 180 weight section to the (A) component 100 weight section, and are the 10 - 100 weight section preferably. 8

[0007] The carbon black of the (C) component used for this invention is a strong nature bulking agent, what is generally used as a reinforcement nature bulking agent of rubber is usable, and especially the kind etc. is not limited. As this carbon black, thermal black, acetylene black, and fur nest black mention, and it is \*\*\*\*\*. The loadings of this component are the 0 - 200 weight section to the (A) component 100 weight section, and are the 10 - 120 weight section preferably. CB

[0008] The silane coupling agent of the (D) component used for this invention carries out the work which strengthens combination with organic system rubber and a silica system bulking agent. The loadings of this component are 0.1 - 10 weight section to the (A) component 100 weight section, and are 1 - 10 weight section preferably. Under in the 0.1 weight sections, an effect will also decrease and this will become in cost and disadvantageous, if the manifestation of the effect of addition is not accepted but 10 weight sections are exceeded. As this silane coupling agent, concretely A screw Trisulfide, a screw (3-triethoxy silyl propyl) A tetrapod sulfide, a screw (2-triethoxy silyl ethyl) A tetrapod sulfide, a screw (3-trimethoxysilylpropyl) Sulfur system silane coupling agents, such as a tetrapod sulfide, 3-mercapto propyltrimethoxysilane, 3-mercapto propyl triethoxysilane, and 3-mercapto propylmethyl diethoxysilane, (2-trimethoxysilyl ethyl) Or alkyl-halide system silane coupling agents, such as 3-chloropropyltrimethoxysilane, 3-chloropropyl triethoxysilane, and 3-chloropropyl methyldiethoxysilane, 3-aminopropyl trimethoxysilane, There are amino \*\* silane coupling agents, such as 3-aminopropyl triethoxysilane, 3-aminopropyl methyldiethoxysilane, 3-(2-aminoethyl) aminopropyl trimethoxysilane, and 3-(2-aminoethyl) aminopropyl triethoxysilane. Also in Kora soil, a screw (3-TORIETOKISHI sill repro pill) tetrapod sulfide and 3-mercapto propyl triethoxysilane are desirable. Moreover, alkyl alkoxysilane can be used as an auxiliary coupling agent. Specifically A tetramethoxy silane, a tetrapod ethoxy silane, methyl trimethoxysilane, Methyl triethoxysilane, dimethyl dimethoxysilane, dimethyl diethoxysilane, Ethyltriethoxysilane, propyl triethoxysilane, propylmethyl diethoxysilane, N-butyltriethoxysilane and n-butyl methyldiethoxysilane, Isobutyl triethoxysilane, isobutyl methyldiethoxysilane, n-hexyl triethoxysilane and n-hexyl methyldiethoxysilane, n-octyl triethoxysilane and n-octyl methyldiethoxysilane, n-decyltriethoxysilane and n-desyl methyldiethoxysilane, Phenyl triethoxysilane, phenylmethyl diethoxysilane, 1, 6-screw (trimethoxysilyl) hexane, 1, 6-screw (triethoxy CA

silyl) hexane, 1, and 6-screw (methyl diethoxy silyl) hexane etc. is mentioned. Methyl triethoxysilane and dimethyl diethoxysilane are desirable also in these.

[0009] (E) The organopolysiloxane of a component is a component which makes the feature of this invention, and carries out the work which raises the dispersibility to the inside of the (A) component of the (B) component. This organic organopolysiloxane is  $R_2Si(OR_6)_2 / R_3Si(OR_7)_2 O_1$  / general formula:  $(R_1SiO_{3/2})_m [2] n [2] p (R_4R_5SiO_{2/2}) q (R_8R_9SiO_{1/2}OH)_r$  (among a formula).  $R_1, R_2, R_3, R_4, R_5, R_9$ , and  $R_{10}$  The monatomic organic group chosen from the amino alkyl group of a 12 or less-carbon number monovalent hydrocarbon radical, the 1st class, the 2nd class, or the 3rd class, an epoxy alkyl group, a meta-chestnut ROKISHI alkyl group, a mercapto alkyl group, and an alkyl-halide machine is shown.  $R_6, R_7$ , and  $R_8$  show a 12 or less-carbon number monovalent hydrocarbon radical or a hydrogen atom.  $m$  is the integer of 5-1,000, and  $n$  and  $p$  are the number of 1-1,000, and the sum of  $n, m$ , and  $p$  is 180 or more.  $q$  is the integer of 20-1,000 and  $r$  is the number of 0-1,000. It is organopolysiloxane expressed. As the inside of an upper formula, and an example of  $R_1, R_2, R_3, R_4, R_5, R_9$ , and  $R_{10}$  Monovalent hydrocarbon radicals, such as a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, i-butyl, t-butyl, n-hexyl machine, c-hexyl machine, a phenyl group, a tolyl group, and a naphthyl group, Organic functional groups, such as the amino alkyl group of the 1st class, the 2nd class, or the 3rd class, an epoxy alkyl group, a meta-chestnut ROKISHI alkyl group, a mercapto alkyl group, an alkyl-halide machine, and an alkylene machine, are mentioned. Moreover, as an example of  $R_6, R_7$ , and  $R_8$ , hydrocarbon groups, such as a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, i-butyl, t-butyl, n-hexyl machine, c-hexyl machine, a phenyl group, a tolyl group, and a naphthyl group, are mentioned. Especially  $R_1, R_2, R_3, R_4, R_5, R_9$ , and  $R_{10}$  have a methyl group or a desirable phenyl group, and  $R_6, R_7$ , and  $R_8$  have a methyl group or a desirable ethyl group from points, such as thermal resistance and a manufacturing cost. In addition,  $R_1-R_{10}$  in 1 molecule may be the same, and they may differ. The number of 5-100 and  $q$  are the number of 20-100, and the number of  $r$  of 5-100 is [ the number of 5-100, and  $n$  / the number of 50-800, and  $p$  ] desirable [ further  $m$  ]. The loadings of this component are 0.1 - 10 weight section to the (A) component 100 weight section, and are 1 - 10 weight section preferably. This is because the property of rubber changes and is not desirable in under the 0.1 weight section if the manifestation of the effect of addition is not accepted but it adds more than 10 weight sections.

[0010] (F) The vulcanizing agent of a component is for stiffening the constituent of this invention, and the vulcanizing agent currently generally used for vulcanization of organic system rubber is used. As this vulcanizing agent, there is organic peroxide, such as sulfur, such as powder sulfur, colloid sulfur, and insoluble sulfur, a benzoyl peroxide, and peroxidation JIKUMIRU, etc. S

[0011] Although the constituent of this invention consists of the above (A) component - (F) components, it is desirable to blend the plasticizer for using rubber in order to improve the moldability of organic system rubber common as a (G) component and processability in addition to these components. As this plasticizer for rubber, there are a paraffin hydrocarbon, a naphthene hydrocarbon, and an aromatic system hydrocarbon, and it is marketed as the plasticizer for rubber, and a process oil. Furthermore, the constituent of this invention is not hindered by carrying out addition combination of antioxidants, such as vulcanizing agent assistants, such as the various additives with which it is made well-known at organic system rubber to carry out addition combination, for example, a zinc white, (zinc oxide), and stearin acid, diphenylamines, trimethyl dihydroquinones, and phenylenediamines, various heat-resistant agents, the reinforcement nature additive, etc., unless the purpose of this invention is spoiled.

[0012] The constituent of this invention is easily obtained by mixing uniformly the above (A) component - (F) components or a (A) component - (G) component. The mixed equipment currently used for manufacture of the conventional organic system rubber constituent as a mixed means is usable.

[0013] After hardening, since it may become rubber excellent in rubber elasticity and the mechanical strength, the above organic system rubber constituents of this invention are suitably used as the use of which this property is required, for example, rubber for tires of an automobile or a bicycle.

[0014]

[Example] Hereafter, the example of this invention is shown. That it is with the section shows the

weight section among an example, % shows percent, Me shows a methyl group, and Et shows an ethyl group. Moreover, the dispersibility of the inside of an example and the silica system bulking agent in the example of comparison was measured as follows.

O The electron microscope photograph of the rubber constituent in which the silica system bulking agent carried out dispersibility manufacture was taken, and the number of the grains of the silica system bulking agent condensed the 2nd order was counted visually. The measurement result showed the grain of the silica system bulking agent condensed the 2nd order by the number per unit area (piece/mm<sup>2</sup>).

[0015]

[Example 1] As the organic rubber 100 weight section which becomes a Banbury mixer from the solution polymerization styrene-butadiene copolymer rubber (ten mol % of styrene contents) 60 section, and the emulsion-polymerization styrene-butadiene copolymer rubber (23.5 mol % of styrene contents) 40 section which contained natural rubber 40% of the weight, the silica impalpable-powder (Japan silica incorporated company make, tradename nip sill AQ) 50 section, the carbon black (thermal black) 40 section, and a silane coupling agent. As the \*\* screw [(TORIETOKISHI) silyl propyl] tetrapod sulfide (BESTS) 4 section, the dimethyl diethoxysilane (DMDES) 1 section as an auxiliary silane coupling agent, and a silica dispersibility improver The organopolysiloxane resin (average molecular weight 15000) 3 section shown by formula 1 (MeSiO 3/2) 10 (MeSiOEtO 2/2) 80 (MeSi(OEt)2O1/2) 10 (Me2SiO 2/2) 40 (Me2SiO1/2OH) 10 is supplied. The aromatic system hydrocarbon plasticizer 35 section, the wax 1 section, the sulfur powder 2 section, the zinc white 5 section, and the stearin acid 2 section were blended, it mixed uniformly, and the organic rubber constituent was prepared. The dispersibility of the silica impalpable powder in the obtained rubber constituent was measured. Moreover, the loss modulus (Tandelta) of the hardened material of this rubber constituent, the complex modulus (E'), and the modulus at the time of 300% extension (300% modulus) were measured. These measurement results were shown in Table 1 which carries out a postscript.

[0016]

[Example 2] As the organic rubber 100 weight section which becomes a Banbury mixer from the solution polymerization styrene-butadiene copolymer rubber (ten mol % of styrene contents) 60 section, and the emulsion-polymerization styrene-butadiene copolymer rubber (23.5 mol % of styrene contents) 40 section which contained natural rubber 40% of the weight, the silica impalpable-powder (Japan silica incorporated company make, tradename nip sill AQ) 40 section, the carbon black (thermal black) 40 section, and a silane coupling agent. As the \*\* screw [(TORIETOKISHI) silyl propyl] tetrapod sulfide (BESTS) 4 section, the dimethyl diethoxysilane (DMDES) 1 section as an auxiliary silane coupling agent, and a silica dispersibility improver The organopolysiloxane resin (average molecular weight 13000) 4 section shown by formula 1 (MeSiO 3/2) 10 (MeSiOEtO 2/2) 80 (MeSi(OEt)2O1/2) 10 (Me2SiO 2/2) 40 (Me2SiO1/2OH) 10 is supplied. The aromatic system hydrocarbon plasticizer 35 section, the wax 1 section, the antioxidant 2 section, the stearin acid 2 section, the zinc white 5 section, the sulfur 2 section, and the vulcanization-accelerator 1 section were blended, it mixed uniformly, and the organic rubber constituent was prepared. The dispersibility of the silica impalpable powder of the obtained constituent was measured. Moreover, the loss modulus (Tandelta) of the hardened material of the obtained rubber constituent, the complex modulus (E'), and the modulus at the time of 300% extension (300% modulus) were measured. These measurement results were shown in Table 1 which carries out a postscript.

[0017]

[Example 3] As the organic rubber 100 weight section which becomes a Banbury mixer from the solution polymerization styrene-butadiene copolymer rubber (ten mol % of styrene contents) 60 section, and the emulsion-polymerization styrene-butadiene copolymer rubber (23.5 mol % of styrene contents) 40 section which contained natural rubber 40% of the weight, the silica impalpable-powder (Japan silica incorporated company make, tradename nip sill AQ) 50 section, the carbon black (thermal black) 40 section, and a silane coupling agent. As the \*\* screw [(TORIETOKISHI) silyl propyl] tetrapod sulfide (BESTS) 4 section, the dimethyl diethoxysilane (DMDES) 1 section as an auxiliary silane coupling agent, and a silica dispersibility improver The organopolysiloxane resin 3 section shown by average

empirical-formula 1 (MeSiO 3/2) 10 (MeSiOEtO 2/2) 80 (MeSi(OEt)2O1/2) 10 (Me2SiO 2/2) 40 (Me2SiO1/2OH) 10 is supplied. The aromatic system hydrocarbon plasticizer 35 section, the wax 1 section, the antioxidant 2 section, the stearin acid 2 section, the zinc white 5 section, the sulfur 2 section, and the vulcanization-accelerator 1 section were blended, it mixed uniformly, and the organic rubber constituent was prepared. The dispersibility of the silica impalpable powder of the obtained constituent was measured. Moreover, the loss modulus (Tandelta) of the hardened material of the obtained rubber constituent, the complex modulus (E), and the modulus at the time of 300% extension (300% modulus) were measured. These measurement results were shown in Table 1 which carries out a postscript.

[0018]

[The example 1 of comparison] In the example 2, the organic rubber constituent was prepared like the example 1 except having not blended the organopolysiloxane resin expressed with a formula 1. The dispersibility of the silica impalpable powder of the obtained rubber constituent was measured. Moreover, the loss modulus (Tandelta) of the hardened material of the obtained rubber constituent, the complex modulus (E), and the modulus at the time of 300% extension (300% modulus) were measured. These measurement results were shown in Table 1 which carries out a postscript.

[0019]

[The example 2 of comparison] In the example 2, the organic rubber constituent was prepared like the example 2 except having used the average empirical formula 3 and the organopolysiloxane shown by 20 (MeSiO 3/2) (MeSiOEtO 2/2) 80 instead of the organopolysiloxane resin expressed with a formula 1. The dispersibility of the silica system bulking agent of this constituent was measured. Moreover, the loss modulus (Tandelta) of the hardened material of the obtained rubber constituent, the complex modulus (F), and the modulus at the time of 300% extension (300% modulus) were measured. These measurement results were shown in Table 1 which carries out a postscript.

[0020]

[Table 1]

	実施例 1	実施例 2	実施例 3	比較例 1	比較例 2
スチレン-ブタジエンゴム	100	100	100	100	100
シリカ	50	40	40	40	40
カーボンブラック	40	90	90	90	90
BESTS	4	4	4	8	4
DMDES	1	0	1	0	0
式 1 の有機ケイ素化合物	3	4	0	0	0
式 2 の有機ケイ素化合物	0	0	3	0	0
式 3 の有機ケイ素化合物	0	0	0	0	4
シリカ分散性	0	0	0	25	15
Tan δ 指数	120	105	108	100	106
E' 指数	81	95	85	100	90
300%モジュラス	121	100	110	100	110

[0021]

[Effect of the Invention] Since the organopolysiloxane which consists of a (A) component - (F) component, and is especially shown by the average empirical formula of the (E) component by this invention is contained, the dispersibility of a silica system bulking agent is good, and it has the feature that after hardening may become the rubber Plastic solid excellent in rubber elasticity and the mechanical strength.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the rubber constituent for treads with which may be simultaneously satisfied of the wet-proof skid nature of a tire, rolling-resistance nature, and abrasion resistance, without falling process nature in more detail about the rubber constituent for tire treads.

[0002]

[Description of the Prior Art] With rolling resistance, a part of turning effort applied to the tire with which the automobile was equipped changes to heat energy, and it generates an energy loss. The greater part of this rolling resistance originates in the hysteresis loss accompanying repeat deformation of a tread, and the bird clapper is greatly accepted as the loss tangent (tan delta) of the rubber constituent which used this hysteresis loss for the tread becomes large.

[0003] On the other hand, since the fuel consumption of an automobile will increase and the air pollution problem by exhaust gas will moreover be amplified if the rolling resistance at the time of a tire run is large, it is requested socially that the rolling resistance of a tire should be decreased, mpg should be cut down and an environmental problem should be solved.

[0004] If it is going to decrease rolling resistance by using the low rubber material of glass transition temperatures, such as natural rubber and a cis polybutadiene rubber, or adjusting the kind of carbon black or softener, loadings, etc. in order to reply to this request In the former, wet-proof skid nature falls remarkably, or in the latter When the microstructure of rubber was especially similar, it was very difficult to satisfy simultaneously these [ which the phenomenon in which wet-proof skid nature and abrasion resistance fall is accepted, and carry out an antinomy to \*\* ] three properties.

[0005] Overthrowing this antinomy relation and holding wet-proof skid nature and abrasion resistance enough also conventionally, the attempt which makes rolling resistance small is made, for example, an organic lithium is obtained as an initiator in JP,3-252431,A, and the pneumatic tire which used for the tread the rubber constituent which comes to blend carbon black with the raw material rubber to which a glass transition temperature makes a principal component a diene system polymer -50 degrees C or more a silica bulking agent, a silane coupling agent, and if needed is proposed. Moreover, it changes into the above-mentioned diene system polymer, a rubber constituent is similarly constituted from JP,3-252433,A using the denaturation polymer which is made to carry out the coupling reaction of the activity diene system polymer which has a lithium-carbon to carbon bond at the molecule end, and the specific silane compound, and is obtained, and the pneumatic tire which used this for the tread is proposed. Moreover, the way nitrogen adsorption specific surface area uses the rubber constituent which blended the silica bulking agent 100 - 250 m<sup>2</sup> / g, and whose dibutyl-phthalate oil absorption are 150-250ml / 100g for a tire tread as a bulking agent which replaces the rubber whose glass transition temperature is 0--80 degree C at carbon black by the copolymer of a conjugated-diene compound and 5 - 50% of the weight of an aromatic vinyl compound is indicated by the Europe public presentation patent EPO No. 501227.

[0006]



[Problem(s) to be Solved by the Invention] By the way, the silica restoration combination which makes the solution polymerization diene system polymer obtained considering an organic lithium as an initiator, raw material rubber like aforementioned JP,3-252431,A was not enough as processability and abrasion resistance, and, in addition, there was room of improvement by it. Moreover, although the molecular weight of the above-mentioned solution polymerization diene system polymer is increased by making a silane compound into a coupling agent, Mooney viscosity is set as the range [ \*\*\*\* ] and the wear-resistant improvement is aimed at in JP,3-252433,A, examination is hardly made about the requirements for improving the processability of silica combination, for example, the molecular weight distribution of polymer. Furthermore, the problem that carry out breakdown and molecular weight tends to fall although the polymer which carried out distributor shaft coupling using the silane compound does not come out like a tin compound is pointed out conventionally. Moreover, the silica combination like EP No. 0501227 publication is charged without static electricity generated in the automobile escaping on a road surface if a tire tread is constituted from this, since electric insulation is high, and it has the fault of occurring electromagnetic interferences, such as a radio noise. A deer is carried out, and the purpose of this invention has good processability compared with silica restoration combination of this conventional type, and it excels in wet-proof skid nature, low rolling-resistance nature, and abrasion resistance, and is in offering the rubber constituent for tire treads with which sufficient conductivity was moreover secured.

[0007]

[Means for Solving the Problem] When this invention persons constituted the rubber constituent for tires combining the solution polymerization diene system rubber obtained by carrying out distributor shaft coupling by the multifunctional compound [ \*\*\*\* ] containing the diglycidyl amino group as a result of repeating research wholeheartedly, in order to solve the above-mentioned technical problem, and a silica bulking agent and carbon black, they find out that the desired end is attained and came to complete this invention.

[0008] Namely, the living polymer obtained by this invention making an organic lithium a catalyst in a hydrocarbon solvent, and copolymerizing styrene and 1,3-butadiene Come to carry out distributor shaft coupling by the multifunctional compound containing the diglycidyl amino group. The independence of the distributor-shaft-coupling conversion solution polymerization styrene-butadiene copolymer rubber which whose weight average molecular weight (Mw) is 500,000 or more, and has the molecular weight distribution (Mw/Mn) shown by the ratio of weight average molecular weight (Mw) and number average molecular weight (Mn) in the range of 2.2-3.2, Or the raw material rubber 100 weight section which the remainder becomes from other diene system rubber components is received, including this copolymer rubber 60% of the weight or more. It is related with the rubber constituent for tire treads which makes a silica bulking agent 10 - 80 weight section, and makes carbon black to more than 25 weight sections, and carries out 40 in all to 100 weight section combination of this silica bulking agent and this carbon black, and is characterized by the bird clapper.

[0009] As a multifunctional compound [ \*\*\*\* ] containing the above-mentioned diglycidyl amino group, diglycidyl aniline, a tetraglycidyl ether meta-xylene diamine, tetraglycidyl ether -1, 3-screw aminomethyl cyclohexane, etc. can be illustrated, for example. By choosing suitably the kind (or the number of functional groups) of these multifunctional compounds, the molecular weight of a living polymer, and both reaction mole ratio, the rubber-like polymer adjusted to the molecular weight and molecular weight distribution after a coupling reaction, or the value of a request of the number of unreacted glycidyl groups can be obtained.

[0010] Weight average molecular weight (Mw) is 500,000 or more among the rubber-like polymer obtained in this way, and the styrene-butadiene copolymer rubber which molecular weight distribution (Mw/Mn) are in the range of 2.2-3.2, and contains the unreacted glycidyl group of a piece at least is suitable especially as a rubber component of this invention. The unreacted glycidyl group which remains in this rubber-like polymer raises the interaction of polymer and a silica bulking agent upwards, and is effective, and 500,000 or more and a high thing have advantageous molecular weight (Mw) for a wear-resistant and low febrile improvement. Moreover, they are the requirements to which molecular weight



distribution (Mw/Mn) are indispensable in latus suppressing the fall of the processability accompanying silica combination or more by 2.2. However, since a heat generation characteristic will fall based on the increase in low-molecular-weight polymer if (Mw/Mn) exceeds 3.2, it is not desirable.

[0011] In order that the distributor-shaft-coupling conversion solution polymerization styrene-butadiene copolymer rubber used in this invention may raise an interaction with a silica further, the feature is in specifying a styrene content and the amount of vinyl combination, and making the pendant machine in a polymer chain increase in addition to the unreacted glycidyl group in a molecule. That is, when setting the amount of vinyl combination of S (mol %) and this butadiene portion to V (mol %) for the styrene content in the polymer chain which constitutes a solution polymerization styrene-butadiene copolymer, especially the thing constituted so that A and B might satisfy simultaneously the relation expressed with a lower formula (1) and (2) is suitable.

$$45 \geq S + 1/2V \geq 25 \quad (1)$$

$$62 \geq S + V \geq 40 \quad (2)$$

In a formula (1), it is difficult for  $S + 1/2V$  to make abrasion resistance and a heat generation characteristic good or more by 45, and it cannot maintain wet-proof skid nature or less by 25. Moreover, in a formula (2), if  $S + V$  becomes 62 or more, the double bond which can construct a bridge will decrease, a bad influence will appear in vulcanization speed, or less by 40, it becomes insufficient [ the amount of pendants ] and a strong interaction with a silica cannot be secured.

[0012] In this invention, like the above, it is independent about the conversion solution polymerization styrene-butadiene copolymer rubber which comes to carry out distributor shaft coupling by the multifunctional compound [ \*\*\*\* ], or it is used, blending with other diene system rubber components so that this may be contained 60% of the weight or more in raw material rubber. Interaction with this rate of a blend sufficient between polymer and a silica at less than 60 % of the weight is not acquired, and the desired end is not attained. As other diene system rubber used here, it is [ cis- / quantity / natural rubber, a synthetic polyisoprene rubber, and ]. -It is / cis- / low / 1, 4-polybutadiene rubber, and ]. -The blend rubber which consists of general-purpose diene system rubber, such as 1, 4-polybutadiene rubber, emulsion-polymerization styrene-butadiene copolymer rubber, and solution polymerization styrene-butadiene copolymer rubber, and these one or more sorts can be mentioned. CA  
Silica

[0013] The rubber constituent concerning this invention is characterized by carrying out 40 in all to 100 weight section content of this silica bulking agent and the carbon black for a silica bulking agent, including 10 - 80 weight section and carbon black more than 25 weight sections per above-mentioned raw material rubber 100 weight section. Although a silica bulking agent is deficient in the improvement effect of wet-proof skid nature in under 10 weight sections and the total quantity of a silica and carbon black is excellent in rolling-resistance nature in under 40 weight sections, rubber does not have intensity and abrasion resistance is missing. If a silica bulking agent exceeds 80 weight sections or the total quantity of a silica and carbon black exceeds the 100 weight sections, processability and rolling-resistance nature will fall.

[0014] Drawing 1 shows the loadings of carbon black, and a conductive relation about the rubber constituent concerning this invention. A vertical axis is a volume-resistivity value. When there is little carbon black so that more clearly than drawing, about the same electric insulation as silica combination is shown. When a tire was constituted from such combination, static electricity generated in an automobile caused radio-noise generating that it is hard to escape on the ground. Then, in this invention, in order to secure the conductivity of a rubber constituent, carbon black is blended more than 25 weight sections per raw material rubber 100 weight section. Especially the kind of carbon black used here is iodine-adsorption-number (IA)65 mg/g, although not limited. They are dibutyl-phthalate oil absorption (DBP) of 90cm<sup>3</sup> / 100 g above. The reinforcement nature carbon black which shows the above colloidal property can secure abrasion resistance simultaneously with conductivity, and is desirable.

[0015] Moreover, a silica bulking agent has the wet method silica more desirable than a dry-process silica usually known as an object for general rubber. As the suitable example, it is a product made from Japanese Silica. Tradename: Nip seal VN3, AQ, Tokuyama Soda Co., Ltd. make Tradename: TOKUSHIRU U, Shionogi & Co., Ltd. make Tradename: Carplex 1120, product made from Mizusawa

Chemistry Tradename: Siluton R-2 grade can be mentioned.

[0016] In addition, of course to the rubber constituent concerning this invention, a well-known vulcanizing agent, a vulcanization accelerator, a vulcanization promotion assistant, a plasticizer, an antioxidant, a silane coupling agent, etc. can be suitably added besides the above-mentioned component. Also in this case, as for a silane coupling agent, it is desirable to add in 5 - 10% of range of a silica fill according to the usual prescription.

[0017]

[Function] In this invention, the rubber constituent which has low febrility and good abrasion resistance is obtained, without being accompanied by the fall of processability, since the multifunctional compound containing the diglycidyl amino group is used for a coupling agent and the molecular weight and molecular weight distribution are adjusted to the specific range about the styrene-butadiene copolymer rubber combined with a silica. Moreover, the interaction of polymer and a silica can be raised, without having a bad influence on vulcanization speed, since the styrene content and the amount of vinyl combination were set as the specific range and the pendant machine in polymer was made to increase in addition to the diglycidyl amino group which remains into a molecule. Moreover, since specified quantity addition of the carbon black was carried out in addition to the silica, the electric insulation of silica combination is canceled and generating of a radio noise is prevented. By using the rubber constituent of this composition for a tread, it became possible to improve the wet-proof skid nature and rolling-resistance nature of a pneumatic tire, maintaining abrasion resistance.

[0018]

[Example] Below, an example and the example of comparison are given and this invention is explained concretely. Table 1 shows the styrene content (S) of the solution polymerization styrene-butadiene copolymer rubber of each coupling-agent conversion, the amount of vinyl combination of the butadiene section (V), weight average molecular weight (Mw), molecular weight distribution (Mw/Mn), and the amount of pendants (S+V and S+1/2 V).

[0019] About the infrared absorption spectrum by which the microstructure of the styrene-butadiene copolymer rubber in Table 1 is measured using FT-IR, the styrene content was calculated by the Hampton technique, the amount of vinyl combination of the butadiene section was calculated by the MORERO method, and it was determined. Weight average molecular weight (Mw) and molecular weight distribution (Mw/Mn) are the values measured by the gel permeation chromatography by using THF as an expansion solvent.

[0020]

[Table 1]

SBRの種類	A	B	C	D	E	F	G	H
S (モル%)	27.3	12.8	21.9	18.9	7.0	18.9	16.8	14.8
V (モル%)	26.2	32.3	28.9	24.3	33.8	17.0	23.3	39.2
S + 1/2 V	40.5	29.0	35.4	31.1	23.9	27.4	28.5	34.4
S + V	53.5	45.1	50.8	43.2	40.8	33.9	40.1	54.0
M <sub>w</sub> (10 <sup>-4</sup> )	68	64	29	70	62	64	61	45
M <sub>w</sub> /M <sub>n</sub>	3.0	2.6	1.5	3.0	2.5	1.4	2.6	1.4
カップ リング剤	テトラグリシジル メタキレンジ アミン	テトラグリシジル -1,3-ビス ミノメチルシクロ ヘキサン	トリエトキシシクロ ロタン	テトラグリシジル メタキレンジ アミン	テトラグリシジル -1,3-ビス ミノメチルシクロ ヘキサン	四酸化ケイ素	テトラグリシジル メタキレンジ アミン	四酸化スズ

[0021] Cis-[ various kinds of distributor-shaft-coupling conversion styrene-butadiene copolymer rubber independence shown in Table 1 or / cis-/ this and ] -It came, whenever it was shown in Table 2, and the rubber constituent which makes blend rubber with 1 and 4-polybutadiene rubber (BR01) raw material rubber, and makes emulsion-polymerization styrene-butadiene copolymer rubber (SBR1712) the criteria rubber of characterization was mixed and prepared by the Banbury mixer in the blending ratio of coal.

[0022] Subsequently, since rolling resistance was related to the shearing loss tangent (tan delta) by the following method again in many properties, such as wet-proof skid nature at the time of using for processability and a tire tread about each above-mentioned rubber constituent, abrasion resistance, and conductivity, this was measured and rolling resistance was evaluated.

Processability -- JIS It applies to K6300 correspondingly and is Mooney viscosity. ML 1+4 (100 \*\*) was measured, the case where the value was 80 or less was made into processing fitness (O mark), and the thing exceeding 80 was made into processing difficulty (x mark).

Wet-proof skid nature -- The British Stanley portable skid circuit tester is used for the frictional resistance to the humid road surface which wet the front face of Safety Walk (Type B) by Sumitomo 3 M company with water, and created it. 38 Rubber Chemical and Technology It measured according to the method given in 840 page, and it carried out indexation, having used measured value of the example 1 of comparison as 100, and it considered as the index by which wet-proof skid nature is evaluated. It is so desirable that a value is large.

Rolling-resistance nature -- Made in the Iwamoto factory VISCO ELASTIC SPECTROMETER It is attached to 5mm angle around and a sample with a thickness of 2mm, and is [ 50Hz and ] 5%.

Indexation of the shearing loss tangent (tan delta) measured at the temperature of 60 degrees C was carried out under the shearing condition, having used the example 1 of comparison as 100, and it considered as the index by which rolling-resistance nature is evaluated. In this case, the one where a value is smaller is desirable.

Wear-resistant -- The run bone abrasion tester made from \*\*\*\*\* Co. is used, and it is JIS. K6264 is followed and they are 3kg of loads, and 60% of slip ratio. It carried out indexation, having used the example 1 of comparison as 100, and the amount of abrasion losses measured under the condition was made into the index of wear-resistant evaluation. The one where a value is larger is desirable.

Conductive -- When direct current voltage was impressed to inter-electrode [ two ] on both sides of a

test piece, the current value which passes along a test piece was measured, and the volume-resistivity value (numeric value which  $\frac{V}{I}$  (ed) voltage with the current which passes along the unit volume of a test piece) which can be found from this was made into the conductive index. The one where a value is smaller is desirable. A result is collectively shown in Table 2.

[0023]

[Table 2]

	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	比較例 1	比較例 2	比較例 3	比較例 4	比較例 5	比較例 6
SBR A	75											
SBR B		75										
SBR C								75				
SBR D									75			
SBR E										75		
SBR F											75	
SBR G			75	75	75	100						
SBR H												100
BR-01 *1	25	25	25	25	25			25	25	25	25	
SBR1712 *2							100					
シリカ (シリカ AQ)	40	40	15	45	65	65		40	80	40	40	40
カーボンブラック N234	30	30	45	25	25	25		30		30	30	30
N339							80					
Si-69 *3	3.2	3.2	1.2	3.6	5.2	5.2		3.2	6.4	3.2	3.2	3.2
プロセスオイル	30	30	30	30	45	45	37.5	30	30	30	30	37.5
加工性	○	○	○	○	○	○	○	○	○	○	×	×
耐水・耐油・耐薬品性	105	100	100	101	102	105	100	102	101	98	100	106
転がり抵抗性	96	91	97	91	95	96	100	92	97	89	95	93
耐摩耗性	100	114	108	110	113	100	100	91	93	116	101	85
体積抵抗 ( $\Omega \cdot \text{cm}$ )	$10^7$	$10^7$	$10^5$	$10^8$	$10^8$	$10^8$	$10^5$	$10^7$	$10^{13}$	$10^7$	$10^7$	$10^7$

\*1) J S R 社製 シスーポリブタジエン、\*2) 油展乳化重合 S B R、\*3) デグサ社製 シランカップリング剤

[0024] As shown in Table 1 and 2, the rubber constituent (examples 1-6) with which are satisfied of the requirements for composition of this invention like the above is equipped with the wet-proof skid nature and abrasion resistance which have good processability in spite of being silica combination, excel [ all ] in rolling-resistance nature as compared with the rubber constituent (example 1 of comparison) which consists of an emulsion polymerization SBR of carbon black reinforcement, and are not inferior to this. Moreover, conductivity is also enough.

[0025] Furthermore, when explained in detail, the example 1 of comparison is a rubber constituent for general treads which consists of an emulsion polymerization SBR (SBR 1712) containing carbon black (N-339), and considered this as the control for characterization. Although the example 2 of comparison is the thing of the same combination composition as examples 1 or 2 except having used the solution polymerization styrene-butadiene copolymer rubber which comes to carry out distributor-shaft-coupling conversion by the TORIETOKISHI chlorosilane and rolling-resistance nature and wet-proof skid nature are improved, that molecular weight (Mw) is also as small as 290,000 originates, and it is inferior in abrasion resistance. Moreover, even if it is filling with combination of only a silica bulking agent the requirements for composition raw material rubber starts this invention even if like the example 3 of comparison, electric insulation is high and serves as a constituent in which abrasion resistance was inferior.

[0026] The example with which the example 4 of comparison has the small value of  $S+1/2 V$  in the microstructure of the distributor-shaft-coupling conversion solution polymerization styrene-butadiene copolymer rubber concerning this invention, and the requirements for the aforementioned (1) formula

are not filled is shown. In this case, although the greatest effect was acquired about improvement of rolling-resistance nature and abrasion resistance, the improvement effect of wet-proof skid nature is not inferior and desirable. The example 5 of comparison and the example 6 of comparison are examples about the copolymer rubber which carried out conversion by other conventional-type coupling agents (a tetrachlorosilane and tin tetrachloride). Like [ rubber / conversion / these ] the example 2 of comparison, although an effective effect is accepted in wet-proof skid nature and rolling-resistance nature, since molecular weight distribution (Mw/Mn) are as narrow as 1.4, processability is inferior, and abrasion resistance is bad in especially the latter. This can be considered to originate in molecular weight (Mw) being 500,000 or less independent rubber constituent, excluding a cis-PORIPUTA diene (BR-01).

[0027]

[Effect of the Invention] As above, in this invention, carry out distributor shaft coupling by the multifunctional compound containing the diglycidyl amino group, and it is obtained. Since the specified quantity of a silica bulking agent and carbon black was blended with the raw material rubber which uses the solution polymerization styrene-butadiene copolymer rubber which has a macro and a microstructure, and makes this a principal component and the rubber constituent was constituted, [ \*\*\*\* ] Processability is good, and is excellent in wet-proof skid nature, rolling-resistance nature, and abrasion resistance, and the rubber constituent for tire treads which moreover has conductivity and does not have fear of radio-noise generating is obtained.

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[Translation done.]